HYGROSCOPIC PROPERTIES OF REWETTED CORN

by

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INTRODUCTION

Moisture is the most important factor influencing deteriorative changes of grains during handling and storage. When grain is sufficiently low (below 13%) in moisture content, it can be stored safely for a long period of time with little deterioration providing that the original grain is in good condition and placed in an adequate storage unit. If the moisture content of the grain is high, grains deteriorate rapidly due to the biological activity of the germ, mold, bacteria, insects and also some enzymatic reactions.

Grain is hygroscopic; in other words, it loses or gains moisture in accordance with the surrounding atmosphere. If it is in contact with liquid water, it will, of course, absorb moisture and increase its moisture content. Grain will also lose or gain moisture depending on the temperature and humidity of the surrounding atmosphere.

There is a moisture movement between grain and surrounding air until moisture equilibrium is reached. Equilibrium is the condition at which moisture ceases to move from the grain to the air or from the air to the grain. Since both air and grain contain water vapor, each exerts a vapor pressure. Vapor moves from a higher pressure to a lower one, so when the the vapor pressure in the grain is higher than that of the surrounding air, moisture moves from the grain to the air and decreases grain moisture. Conversely, when the air vapor pressure is higher than that of the grain, the grain is wetted and moisture increases.

Since there are a number of factors (grain and air temperature, relative humidity, length of storage time, condition of grain, previous history of grain, conditions and types of storage, etc.) other than moisture content of grain that influence grain quality changes, it is almost impossible to state a definite moisture limit at which a given grain may be stored safely and above which deterioration may occur. However, in general, the limit of moisture for safe storage of grain is the moisture content of grain which is in equilibrium at 70 percent relative humidity.

Drying temperatures may have a significant effect on grain quality. Excessively high temperatures in corn causes increased breakage, stress cracking, kernel discoloration, and lead to a decrease in milling yield and protein quality.

There is more marketable flour, and less water, in a bushel of dry wheat than in a bushel of wet wheat. However, the current grading system does not provide for any premium for grains drier than the maximum requirements of the grade. On the other hand, there is a discount for wetter grain.

For instance, grain weight changes about 1.15 percent with each point of moisture above or below standard. When moisture is one point below market, the loss in weight, and therefore market value, is about 1.15 percent. However, when moisture content is one point high, the loss in value is only 0.85 percent because of the 2 percent wet grain discount is offset by the 1.15 percent increase in weight.

Tables below will demonstrate this inequity;

Table 1. Market Standard Moisture Content.

US No 2 Corn	15.5%
US No 1 Soybeans	13.0%
Wheat	13.5%

From Reichenberger (1982).

Table 2. Approximate Net Discounts (Loss) in Value when Moisture is:

	LOW	HIGH
1%	1.15%	0.85%
2%	2.30%	1.70%
3%	3.50%	2.50%
4%	4.60%	3.40%
5%	5.80%	4.20%

From Reichenberger (1982).

These tables show that the market gives its highest price for grain delivered at the market standard moisture content, but it also shows that with a wet grain discount rate of 2 percent per point, a farmer delivering dry grain is paying a bigger penalty than his neighbor hauling wet grain.

It is very hard for man to match nature's system of drying and preserving the grain. Depending on the weather, (Dry, hot winds rolling through the fields), many times farmers harvest when grain is already overdried.

When farmers began restoring moisture to the overdry grain before marketing; representatives of the grain marketing trade became concerned and contacted the Food and Drug Administration for legal ruling.

Pressed by the increasing interest in grain rewetting, the Food and Drug Administration issued an opinion in spring 1982 stating that the addition of liquid water to grain to increase its bulk or weight to improve its value is illegal.

Some economists agree that paying for grain based on its dry matter is certainly one alternative that would remove the incentive for adding water to grain. The problem with this solution, that grain industries foresee, is that over-dry grain breaks up in handling. Then, if one change is made, they may end up having to make other changes that make the system more complicated. If they buy dry matter and more over-dry corn comes in, they will have to make more changes to counterbalance that.

The way water is added back to the grain is; 1) Blending wet and dry grain together, 2) Aerating bins in humid weather or 3) Directly adding water. The latter of these methods is the most practical but also the most controversial.

Since some researchers and grain industry spokesmen question the storability of rewetted grain; the present study is to find a method to determine if over-dry grain has been rewetted or not.-

The sorption of water vapor and liquid water by corn is of specific interest to this study. The basic experimental techniques utilized are: a) the measurement of equilibrium moisture content for non-rewetted and rewetted corn; b) the measurement of the bulk density for non-rewetted and rewetted corn and c) the establisment of a linkage between these measurements and rewetting.

LITERATURE REVIEW

I. General Concepts of Adsorption

Hunt and Pixton (1974) classify water held in grains into three kinds: absorbed, adsorbed, and bound water. The term absorbed water applies when a quantity of water is loosely held inside the grain or in the intermolecular spaces by capillary forces. The characteristics of this water are thought of to be the same as those of common water, and it is sometimes termed free-water.

Water is said to be adsorbed when it is held in the grain by molecular attraction, being closely related to the adsorbing materials and being held more firmly. Physically adsorbed water is held in the system by van der Waals forces.

Bound water or chemically adsorbed water is held in the grain by very strong chemical forces, and it is a chemical union with the adsorbing materials. Large quantities of energy are required to break the chemical bonds, and this bound water usually remains within the grain after common drying.

The equilibrium moisture of dry grain may be pictured as the physical adsorption of a vapor on a solid.

Adsorption occurs as a result of the interaction between the field of force at the surface of the solid and the molecule of water vapor. To grasp the relationships involved in physical adsorption, one may picture a porous solid exposed to vapor. The weight of the solid will increase with time and finally will come to equilibrium with the vapor.

The solid is known as the adsorbent and the vapor the adsorbate. It is usual to carry out the measurements with the adsorbent maintained at a fixed temperature and the relationship between the adsorption "x" (i.e. the amount of water adsorbed) and the vapor pressure P of water vapor in adsorbate, is referred to as an adsorption isotherm.

Adsorption is to be distinguished from "absorption" which involves penetration of the gas and liquid into the structure of the solid by some process of diffussion. Often adsorption and absorption occur simultaneously in porous adsorbents and it is not always easy to identify them with certainty.

It was first shown by McBain (1910) that solid can take up gases in many ways other than causing them to adhere to the outer surface (adsorption) and he introduced the general form "sorption" to include all ways in which the gas is taken up by the solid. Therefore it may be pointed out that adsorption is a particular mechanism of sorption and does not include other mechanisms such as absorption or diffussion.

II. Physical Adsorption and Chemical Adsorption

Adsorption is considered to be a consequence of the field force at the surface of the adsorbent, which attracts the molecules of the adsorbate. The forces of attraction in the adsorbent are mainly of two types, physical and chemical, which cause physical (or van der Waals) adsorption and chemisorption (or activated sorption) respectively.

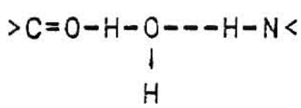
Chemisorption is normally characterized by much stronger binding forces, larger heat of adsorption, and an increased reactivity of the adsorbed molecules.

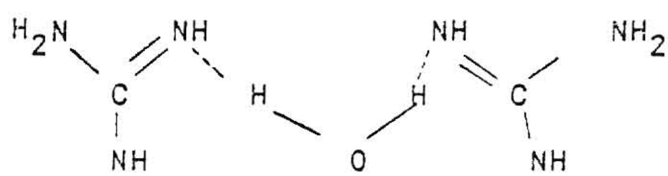
Many investigators agree that the adsorption of water vapor by cereal grains and their products is entirely van der Waals type of adsorption (Brunauer (1943)).

Physical adsorption is caused by intermolecular forces between molecules of water vapor and the surface of the adsorbent (polar sites of the adsorbent). In general polar molecules such as H_2O, NH_3 and alcohol, or molecules posessing the following polar groups, $-NH_2$ $-NH-$, $-OH$, $-COOH$, $CONH_2$ etc., are considered to be sorptive sites on the adsorbent because the positive and the negative charges in the above molecules are not symmetrically distributed. Brunauer (1943) stated that the formation of physically adsorbed layers, may be similar to the condensation of a vapor to form a liquid. The heat of physical adsorption is not only of the same magnitude as the heat of condensation but physically adsorbed layers, particularly those which are many molecular diameters thick, also behave in many respects as a liquid.

The availability of sorptive sites on the surface of the adsorbent of water vapor is the main factor affecting the sorption properties of an adsorbent. Eley and Leslie (1963 and 1964) found some evidence of molecular shrinkage on the complete drying of the adsorbent. Seehof et al. (1953) suggested the mechanism of water molecule binding to be the the cooperative binding of one molecule between two adjacent polar groups. Usually in adsorption work, the adsorbent is dried under high vacuum or activated at high temperatures before an adsorption isotherm is obtained. Now consider these models of water molecule binding between two polar groups:

Prior to activation or drying:

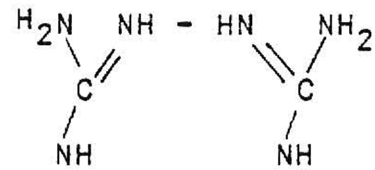




(polysacharide hydroxyl)   (protein)

On activation or drying in high vacuum, the above model may become;

>C=O-HN<



If water molecules between adjacent polar groups are removed in high vacuum or at high temperature, two adjacent polar groups may approach each other and consequently the distance between the two becomes so small that a water molecule could not get between them again, or two adjacent groups might be held to each other by hydrogen bonds. Thus two polar sites become virtually inaccesible to water sorption. Therefore reduced availability of polar sites on the surface of the adsorbent in the adsorption process would be expected. The literature reports that when an adsorbent is wetted, the formation of cracks may be observed radiographically, (Grosh and Milner (1959) and Milner and Shellenberger (1953)). Usually prior to obtaining the desorption isotherm, the adsorbent is wetted. If the wetting results in the formation of cracks in the adsorbents an increase in the surface area and number of sorption sites for desorption would be expected. Such chemical and physical factors would alter the availability of sorptive sites on an adsorbent.

III. Isotherms

The amount of water that can be adsorbed by grains is studied by means of the isotherm. An isotherm is a curve that describes the amount of water in a substance at a particular temperature as a function of the equilibrium vapor pressure, water activity, or relative humidity. The equilibrium relative humidity (E.R.H.) is defined as follows:

$$ERH = \frac{\%\ Relative\ Humidity}{100} = \frac{P}{P_o} \qquad [1]$$

where P is the vapor pressure exerted by the water vapor in the air at a given temperature, and P_o is the saturation vapor pressure of water at the same temperature.

Grain can reach equilibrium statically or dynamically, depending on whether there is a flow of air past the grain. For a great number of isotherm determinations cereal grains are allowed to reach equilibrium statically, in containers with different concentrations of sulfuric acid or salt solutions which exert different vapor pressures. In most grain systems the material reaches equilibrium dynamically since a flow of air is passed through the grain mass. Dunstan et al (1973) stated that in general, the dynamic equilibrium seems to be a little higher than the static equilibrium moisture content.

If water is added to the grain while approaching equilibrium, the curve is referred to as a sorption isotherm; or if water is removed from the grain while approaching equilibrium is called desorption isotherm.

Desorption phenomena is applicable for drying while adsorption or sorption data are more generally applicable to problems in storage.

A. Types of Isotherms

Various types of isotherms are presented in the literature. Brunauer (1943) proposed a classification of isotherm types which has been widely accepted by other investigators.

His classification includes five principal types according to shape and characteristics.

They are designed by roman numbers I to V. The Type I curve is known as the Langmuir's adsorption isotherm or van der Waal's adsorption. Type I isotherm covers monolayer adsorption, and it sometimes describes the initial parts of Type II and IV isotherms.

Type II isotherm is called the S-shaped or sigmoid curve, and it describes the adsorption of water vapor by most cereal grains and their products.

Type III isotherm is related to Type II since both cover multimolecular adsorption and they indicate that adsorption increases indefinitely as the saturation vapor pressure is approached. Type IV and V isotherms describe the adsorption on highly porous adsorbents, and the two suggest that the maximum adsorption tends to have a finite value at some point near the saturation pressure of the gas.

B. Isotherm Equations

Several isotherm equations have been developed by a number of investigators.

Some of the most widely used are:

1. The B-E-T Equation:

This theory was first postulated by Brunauer, Emmett and Teller (1938) and is based on the assumption that the same forces that produce condensation are also responsible for the binding energy of multimolecular adsorption.

The isotherm equation derived is;

$$\frac{V}{V_m} = \frac{CP}{(P_o - P)(1 + (C - 1)\frac{P}{P_o})} \qquad [2]$$

where P= an equilibrium pressure

P_o= the saturation pressure at a given temperature

V_m= the volume or amount of gas adsorbed when the entire adsorbent surface is covered with a complete monomolecular layer

C= constant.

The value of the constant C is given by the following equation:

$$C = \frac{a_1 \ b_2}{b_1 \ a_2} \ e^{\frac{(E_1 - E_L)}{RT}} \qquad [3]$$

where a_1, a_2, b_1, b_2 = constants

$E_1 - E_L$ = net heat of adsorption of the first layer.

The B-E-T equation is the most widely used in adsorption studies because it was derived by a sound and rigorous theoretical approach, and it yields a useful two constant equation from which surface areas and approximate heat of adsorption can be calculated readily.

2. Smith Equation:

Smith (1947) proposed the following isotherm equation to fit isotherms of high polymers.

$$W = W_b - W' \ln\left(1 - \frac{p}{p_o}\right) \qquad [4]$$

where W = moisture content

W_b and W' = constants

$\frac{p}{p_o}$ = equilibrium relative humidity.

3. Henderson Equation:

Henderson (1952) developed an isotherm equation and tested its validity with agricultural materials.

The equation developed is;

$$1 - \frac{P}{P_o} = \exp(-KTM^n) \qquad [5]$$

where $\frac{P}{P_o}$ = equilibrium relative humidity, in decimal

T= absolute temperature

K and n = constants

M = equilibrium moisture content, dry basis, decimal.

4. Chung and Pfost Equation:

Chung and Pfost (1967) developed the following equation:

$$\ln \frac{P}{P_o} = \frac{-A}{RT} \exp(-BM) \qquad [6]$$

where A and B = constants

R = universal gas constant = 1.98 Btu/lb.mole-^oR

T = absolute temperature in degrees Rankine

$\frac{P}{P_o}$ = equilibrium relative humidity in decimal

M = equilibrium moisture content in decimal basis.

All isotherm equations were transformed into linear forms, and their conditions of applicability to grain sorghum data were given in Table 3. These equations show approximately the same range of applicability for many other cereal grains.

The equation from Brunauer et al. (1938) could be sucessfully applied only to relative humidities below 43 percent.

Table 3. A Summary of Four Isotherm Equations.

Equation	Equations in linear form $Y = A + B' X'$				Applicable range of relative humidity (percent)
	Y	A	B'	X'	
B-E-T (1938)	$\frac{P/P_o}{V(1 - P/P_o)}$	$\frac{1}{V_m C}$	$\frac{P}{P_o}$	$\frac{C-1}{V_m C}$	2-43
SMITH (1947)	M	W_b	$-W'$	$\ln(1 - \frac{P}{P_o})$	43-90
HENDERSON (1952)	$\ln(\ln(1 - \frac{P}{P_o}))$	lnKT	n	ln M	2-90
CHUNG AND PFOST (1967)	$\ln(-RT(\ln P/P_o))$	lnA	B	M	2-90

Range available $r = \pm$ at least 0.98

The Smith equation is applicable only in the 43 to 90 percent relative humidity range.

Equations by Chung and Pfost, and Henderson were applicable to a wide range of relative humidities.

IV. Hysteresis

Desorption isotherms generally show higher equilibrium moisture contents than the adsorption isotherms for the same relative humidities. Thus, the equilibrium moisture content of a product can have two values depending on whether adsorption or desorption is taking place. This phenomenon is called hysteresis.

Several investigators have proposed theories to explain the hysteresis phenomenon. Smith (1947) suggested that hysteresis is due to swelling, which increases the surface area of the adsorbent and has its effect on its structure.

Chung and Pfost (1967) stated that the difference is due to the fact that more sorptive sites are available during desorption than during adsorption. Chung and Pfost also found that for wheat the hysteresis effect dissappears in the third adsorption-desorption cycle. They suggest that the chemical and physical structure may become so stable that no further molecular shrinkage or crack formation occurs.

Hart (1964) also found that as temperature increases the hysteresis effect decreases.

V. The Importance of Bulk Density

The United States Grain Standards Act was passed by Congress in 1916. The first standards established under the act were for corn. Various changes have been enacted in the standards since that time (USDA, 1963).

The value of the bulk density as a measure of corn quality was not questioned until the practice of harvesting high-moisture shelled corn and drying it became widespread. Selling large quantities of high moisture corn has also emphasized the problem of specifying corn quality in part by bulk density.

The importance of bulk density increased considerably during the 1970 corn season.

Hall (1972) states that the final test weight after drying is affected by the initial moisture content, drying temperature, amount of overdrying, variety blight resistance, kernel damage, and other unknown factors. In an experiment performed by Hall (1972) it was found that shelled corn increased considerably in bulk density during drying. The bulk density increase was less at the higher temperatures than it was at the lower temperatures. Hand shelled samples representing zero kernel damage, reached a higher bulk density during drying than combine shelled samples. As corn is harvested later in the season its maximum bulk density decreases probably due to weathering. The varietal effect was very pronounced, especially for the blighted corn.

Hall also states that it is unfortunate that the test weight determinations are used as a quality measurement for wet shelled corn. As wet corn is dried its coefficient of friction on the surface is decreased. This permits a closed packing of the kernels in the measured volume. Using the bulk density of shelled corn as a quality measurement is questionable at best. If all the samples were checked at a common dry moisture content of 15.5 percent as an example, the bulk density might be of some value as a measure of kernel density.

OBJECTIVES

The overall objective for this study was to compare hygroscopic properties between rewetted and non-rewetted corn. Specific objectives are:

1. To determine isotherms for rewetted and non-rewetted corn at room temperature in order to observe the difference in moisture content between them.

2. To investigate the effect of three different initial moisture levels on hygroscopic properties of rewetted and non-rewetted corn.

3. To investigate the effect of six different drying temperatures on equilibrium moisture content before and after rewetting.

4. To investigate how those drying temperatures and moisture levels affect bulk density before and after rewetting.

5. To fit the data to Chung-Pfost equation.

MATERIALS AND METHODS

Fresh yellow shelled corn purchased on October 13, 1982 from a COOP elevator at Saint Mary, Kansas was used for this test after removing the dockage. Equilibrium moisture content and bulk density (test weight per bushel) of corn were measured at various test conditions.

A static method, with a sulfuric acid solution to maintain a constant relative humidity, was employed to determine the equilibrium moisture content at a constant temperature.

Wide mouth, 500 ml flasks were filled with about 200 ml of various concentrations of sulfuric acid solutions. Each concentration of sulfuric acid created a different relative humidity (Table 4). The range of relative humidities examined were from 25% to 90%. Samples of grain (20 to 30g) placed in fine wire screen were suspended above the solutions in the sealed flasks. Then the sealed flasks containing the samples were left at a controlled ambient temperature of 25^{o}C. Under the above conditions an equilibration period of 7 days was found to establish moisture equilibrium.

The preparation of sulfuric acid solutions was critical in this experiment. It was neccesary to know what concentration of H_2SO_4 produced the relative humidities needed.

Since the concentration of commercially available H_2SO_4

comes in a range of 95-98% the exact concentration of H_2SO_4 being used had to be determined.

Initial density was determined by weighing a known volume of H_2SO_4 on an analytical balance. Density was calculated by dividing the weight by the volume of the small sample of H_2SO_4. The initial density was 1.82975 g/ml. The initial concentration was found to be 96% by using reference tables (Perry (1950)).

The saturation vapor pressure was obtained from reference tables (Perry (1950)) at 25°C. Knowing what relative humidities are needed the vapor pressures could be calculated. The various concentrations of sulfuric acid at those vapor pressures could be obtained from reference tables. Once the initial concentration was obtained we could get any of the other concentrations by carefully diluting with water.

Table 4. Relative Humidity-Sulfuric Acid Concentration Relationship at 25°C.

Relative Humidity	H_2SO_4 by weight
25%	55.9%
35%	50.9%
50%	43.4%
65%	36.0%
75%	30.4%
90%	18.5%

Table 4 shows the concentrations of H_2SO_4 corresponding to the desired relative humidities at 25°C.

Moisture contents of grain were determined by the standard air-oven method. For this, whole kernels of corn were dried for 72 hours at 103°C.

Bulk density of samples were measured before drying, after drying, and after rewetting by a standard Boerner weight-per-bushel tester. Three replications were taken each time. The standard procedure outlined in Boerner and Ropes (1922) was used for most bulk density determinations. Due to shortage of sample at the end of the experiment only 500 g were available to measure bulk density. Since 1000 g were required by the standard method to fill the measuring volume, a smaller volume was used and a correction factor was calculated. The results, using the slightly different method were fairly accurate for most measurements.

The initial moisture content of the corn was 18.44% (wet basis.) The samples were dried to about 15%, 13% and 11% m.c. in an oven at 5 different temperatures (ranging from 70°F (21°C) to 210°F (99°C)). When the desired approximate moisture was reached the samples were placed above the sulfuric acid solutions to obtain equilibrium moisture contents at room temperature. Two replications were taken.

The samples dried to about 15%, 13% and 11% m.c. were rewetted by absorption. The amount of liquid water added varied with the level of rewetting, e.g. samples rewetted from 13% to 15% m.c. needed less water than the samples rewetted from 11% to 15%. Immediately after the water was added, the bottles containing the samples were vigorously shaken. The bottles were shaken periodically for the first few hours. The samples were left in repose for two time periods -24 hours and 48 hours. After the period the samples were placed in the wire screen basket above the sulfuric acid solutions. After a week above the sulfuric acid solutions the samples reached equilibrium. Moisture content was then determined using the air-oven method.

A second portion of the initial material at 18.44% m.c. was prepared as a control replicate. It was dried by ambient air at 25°C and 38% R.H. It took approximately 3 days to reach 15%, 4 days to reach 13%, and 7 days to reach 11% m.c. These samples were also rewetted by adsorption and rewetting by absorption.

One hundred eight sorption tests were conducted for studying the effects of three factors- initial moisture content, drying temperature and relative humidity on the equilibrium moisture content.

One hundred forty four absorption tests were conducted for studying the effects of initial moisture content hours in rest before testing for equilibrium moisture, drying temperature, and relative humidity on the equilibrium moisture content. In these tests samples were tempered before subjecting to equilibrium test.

Only the effects of initial moisture content and drying temperature on bulk density were examined.

Factors and their levels investigated are summarized in Table 5.

Table 5. Experimental Design

NON-REWETTED CORN

Sample Initial Moisture Content (wet basis)	Drying Temperature °F (°C)	Relative Humidity %
11%	70 (21)	25
13%	120 (49)	35
15%	150 (66)	50
	180 (82)	65
	210 (99)	75
	natural air dried	90

REWETTED CORN

Rewetted from-to (Moisture Content)	Tempering Time (hours)	Drying Temperature °F (°C)	Relative Humidity %
11% to 15%	24	70 (21)	25
13% to 15%	48	120 (49)	35
		150 (66)	50
		180 (82)	65
		210 (99)	75
		natural air dried	90

RESULTS AND DISCUSSION

I. Equilibrium Moisture Content Analysis

The experimental equilibrium moisture contents at three different initial moisture content levels (15%, 13% and 11%) and six different drying temperatures (natural air dried, 21°C, 49°C, 66°C, 82°C, and 99°C) for non-rewetted and rewetted corn are tabulated in Tables 6 and 7 in Appendix.

In order to investigate the reproducibility of the equilibrium moisture content measurements two replications were conducted. The results of the EMC measurements showed good reproducibility of data. The statistical tests also showed (Tables 8 and 9) that there are no significant differences between replications 1 and 2, therefore they can be combined.

A. Non-Rewetted Corn:

The isotherms at 25°C of natural air dried corn and corn dried at 66°C, and 99°C for before rewetting are shown in Figures 1, 2 and 3 respectively.

Figure 1 shows that there is little difference among EMC at 15%, 13% and 11% initial moisture content when corn is naturally air dried, for instance at 75% R.H. the EMC at 15% initial moisture corn is higher than 13% initial moisture corn by 0.28% and the EMC at 13% initial moisture corn is higher than 11% initial moisture corn by 0.36%.

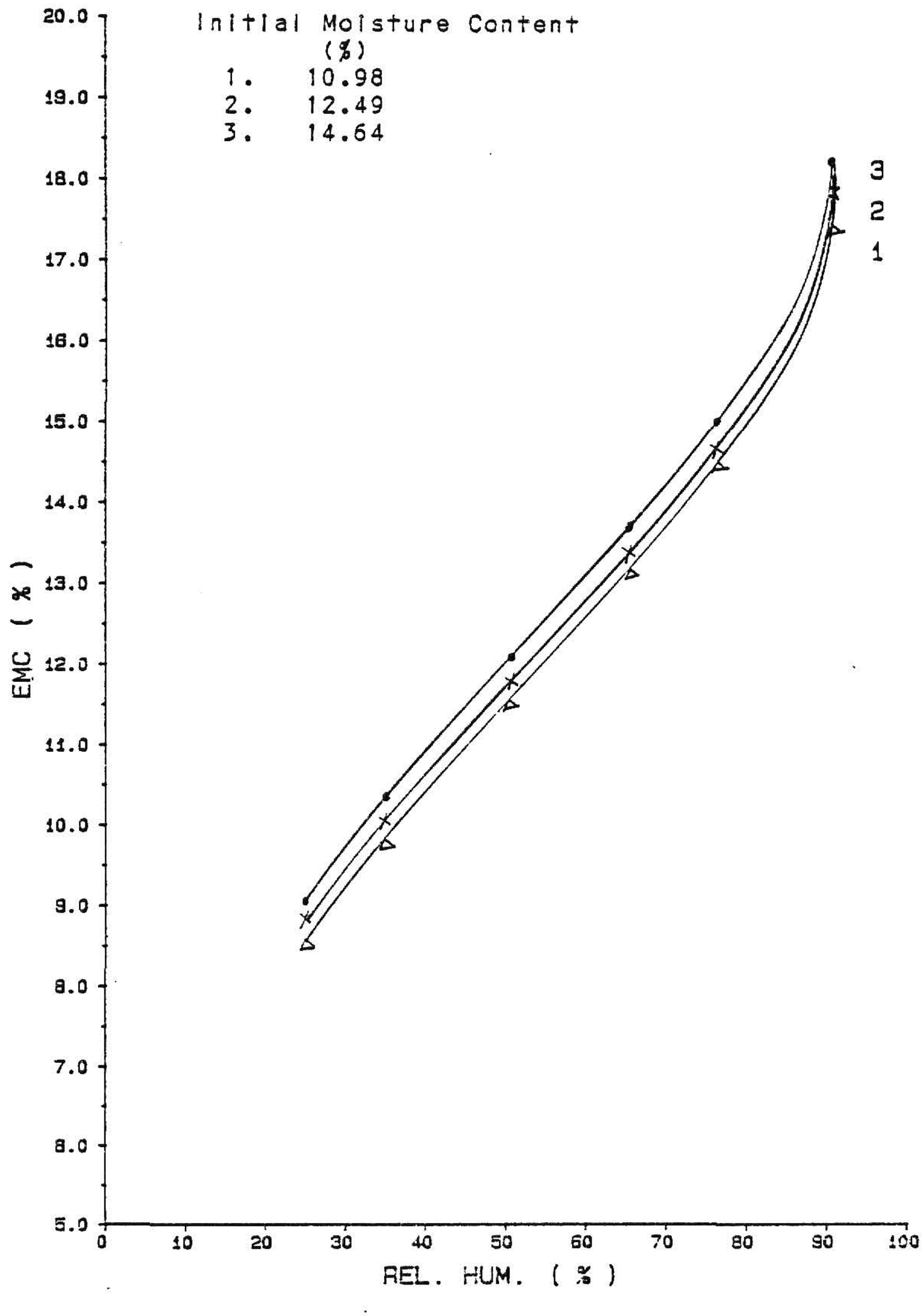


Figure 1. Isotherm curves at 25°C of naturally dried corn for three initial moisture contents before rewetting.

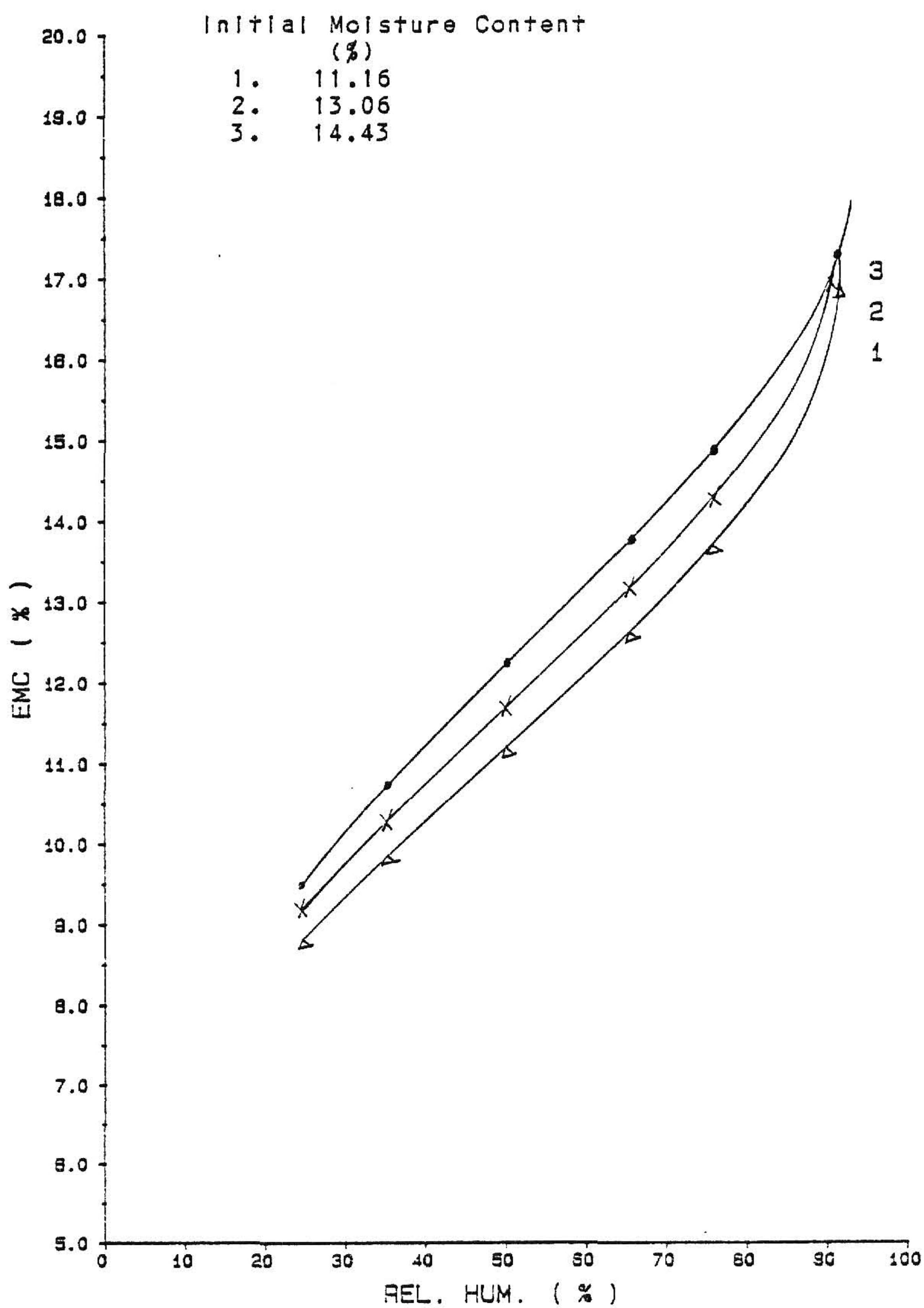


Figure 2. Isotherm curves at 25°C of corn dried at 150 F (66°C) air for three initial moisture contents before rewetting.

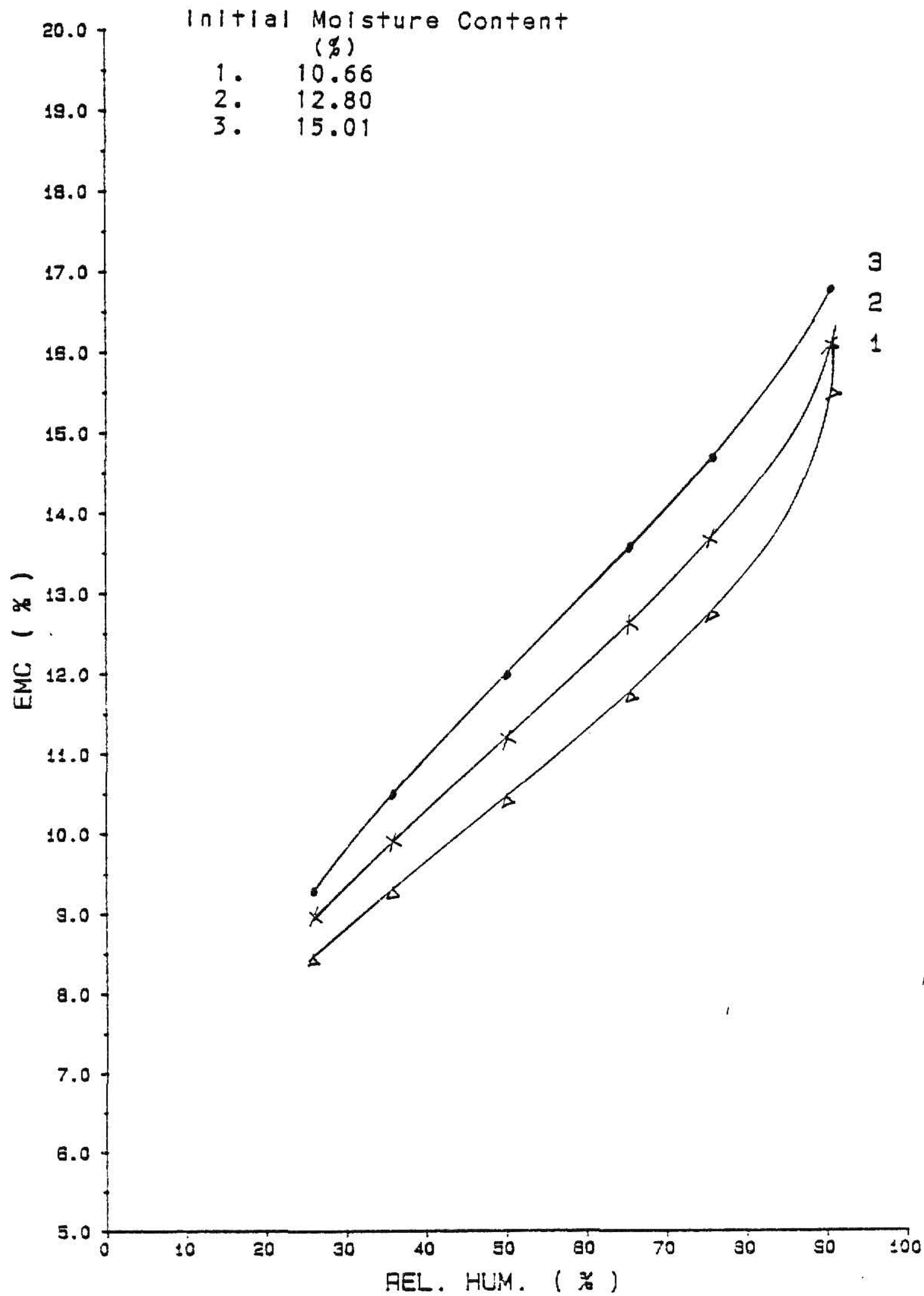


Figure 3. Isotherm curves at 25°C of corn dried at 210 F (99°C) air for three initial moisture content before rewetting.

Table 8. Analysis of Variance all Variables Included for EMC of Corn before Rewetting.

Source	D.F.	SS	F	
Drying temp	5	5.5996	18.07	**
Rel.Hum.	5	1807.9836	5835.79	**
Level [a]	2	23.6110	190.53	**
Rep	1	0.0017	0.03	N.S.
Temp*Rel.Hum.	25	7.1655	4.63	**
Temp*Level	10	4.2552	6.87	**
Rel.Hum*Level	10	4.4304	7.15	**
Error	158	9.7282		
Total	215	1862.7752		

N.S. Not significant
** Significant at the 0.01 level
a. levels=initial moisture content.
Model: $EMC = C_1 t + C_2 RH + C_3 m.c. + C_4 Rep + C_5 t*RH + C_6 t*m.c. + C_7 RH*m.c. + \epsilon$

When corn was dried at 66°C (Figure 2) the differences between EMC at 15% and 13% initial moisture corn at 75% R.H. is 0.31% and EMC of 13% initial moisture corn is higher than EMC of 11% initial moisture corn by 0.52%.

When corn is dried at 99°C (Figure 3) the differences between EMC of 15% and EMC of 13% initial moisture corn at 75% R.H. is 0.75% and EMC of 13% initial moisture corn is higher than EMC of 11% initial moisture corn by 1.08%.

Therefore, it was concluded that as the drying temperature increases the differences between the EMC reached by corn at the initial moisture contents of 15%, 13% and 11% increases. The isotherm curve at 15% initial moisture corn is always above the isotherm curve at 13% initial moisture corn and the isotherm curve at 13% initial moisture corn is always above the isotherm curve at 11% initial moisture corn.

Since the isotherm curves at 15% initial moisture corn stayed fairly constant at any drying temperature it was found that the 11% and 13% isotherm curves shifted downwards as the drying temperature increases.

It was also found that in the relative humidity range of 50% to 75% the differences between the EMC of 15%, 13% and 11% initial moisture corn are more pronounced than at any other relative humidity. The most differences between equilibrium moisture contents reached by 15%, 13% and 11%

initial moisture corn was observed at 75% R.H.

Statistical analysis shows that, in general, at every drying temperature 15% initial moisture corn differs from 11% initial moisture corn. Fifteen percent also differs from 13% at the high drying temperatures (82°C and 99°C); however, 13% does not differ from 11% at any drying temperature.

When comparisons are made among drying temperatures in a fixed initial moisture content, the following results were observed:

For the initial moisture content of 11% very small differences among drying temperatures existed at relative humidities of 25%, 35% and 50%. At 65% and 75% the differences were with the highest drying temperature, and at 90% is where the differences among drying temperatures is most noticeable. Specially the lowest drying temperatures (natural air dried and 21°C) differ very much from the high drying temperatures (82°C and 99°C); for 13% initial moisture corn the differences among drying temperatures start to decrease and they only prevail at the high relative humidities; and for 15% drying temperatures did not have as much effect on equilibrium moisture. Only at the highest relative humidity (90% R.H at 99°C) had lower EMC than the other drying temperatures.

Thus it can be concluded that if the corn is overdried to about 13% or below and the drying temperature is kept above 66°C there are significant differences in the EMC of corn overdried or not and EMC of corn dried at high drying temperatures and low drying temperatures.

The results so far shown can be explained by the molecular shrinkage theory. In this work there are two factors that definitely can change the physical structure of corn; drying temperature and initial moisture content. These two factors decrease the number of sorptive sites available for adsorption. That is why differences appear to show when adsorption began (which is above 50% R.H. in most cases). Therefore when the drying temperatures are very high the sorptive sites available for adsorption decrease considerably. Likewise, when corn is overdried to 13% and below, the grain physical structure changes are irreversible consequently reaching lower equilibrium moisture contents.

Statistical analysis (Table 8) also show that before rewetting the differences in EMC values among initial moisture levels are more pronounced than the differences in EMC values among drying temperatures.

B. Rewetted Corn:

Figure 4 shows that the isotherm curves at 25°C of naturally dried corn when rewetted from 11% to 15% m.c. do not differ very much from the isotherm curves of corn rewetted from 13% to 15%. The same is shown in figure 5 for corn dried at 66°C air. Yet in figure 6 the differences between EMC of corn rewetted from 11% to 15% and EMC of corn rewetted from 13% to 15% is about 1% in most cases. Even though the differences between corn rewetted from 11% to 15% were small for natural air dried corn and corn dried at 66°C the isotherms for corn rewetted from 13% to 15% was always above the isotherm for corn rewetted from 11% to 15% at all drying temperatures for either rewetting time.

The results showed that when the drying temperatures were natural air dried, 21°C, 49°C, and 66°C the EMC reached by corn rewetted from 11% to 15% and corn rewetted from 13% to 15% differ very little. However, at 82°C and 99°C the EMC reached when corn was rewetted from 11% to 15% was lower than that reached when corn was rewetted from 13% to 15%. Yet, the difference was not too much (about 0.5-1.0%), therefore, it cannot be affirmed that these differences are not random error. Nevertheless, statistical tests affirm that at 82°C and 99°C these values do differ.

Tempering times 1 and 2 were not significantly different from each other at any drying temperature. Statistical tests also found them not significantly different in Table 9.

However there is a tendency for tempering time of 48 hours to be a fraction of a percent higher than 24 hours at all relative humidities when corn is rewetted from either 11% to 15% or 13% to 15% at all drying temperatures. When the EMC values of corn rewetted from 11% to 15% were compared among drying temperatures it shows that the differences are small when corn is naturally air dried (Figure 4) and corn dried at 66°C (Figure 5) are compared; the isotherm curves of corn dried at 66°C shows slightly lower than the isotherm curve of natural air dried corn. When natural air dried corn (Figure 4) and corn dried at 99°C (Figure 6) are compared; the isotherm curve of corn dried at 99°C also shows lower than the isotherm curve of natural air dried corn but these differences are also small (less than one percent).

Likewise when the EMC values of corn rewetted from 13-15% were compared among drying temperatures it shows that the differences among low, middle and high drying temperatures are even smaller than for corn rewetted from 11% to 15% and the isotherm curves tend to overlap rather than to shift downwards as for the previous cases.

C. Comparison Analysis between Rewetted and Non-Rewetted Data.

Table 10 through 13 and Figures 7 through 9 show how that EMC of rewetted and non-rewetted corn differ. Data for some other cases are given in Tables 6 and 7 of the Appendix.

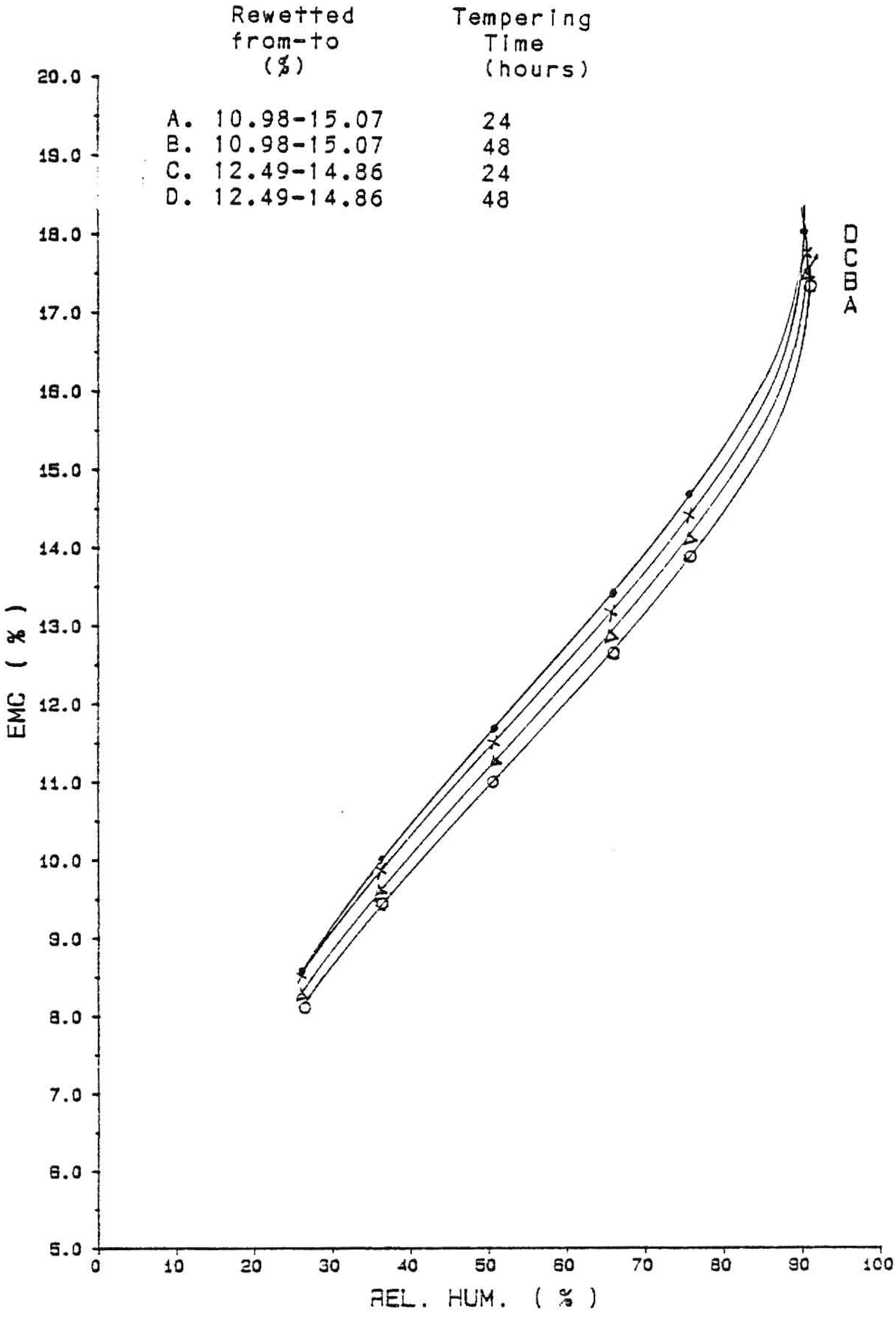


Figure 4. Isotherm curves at 25°C of naturally dried corn after rewetting.

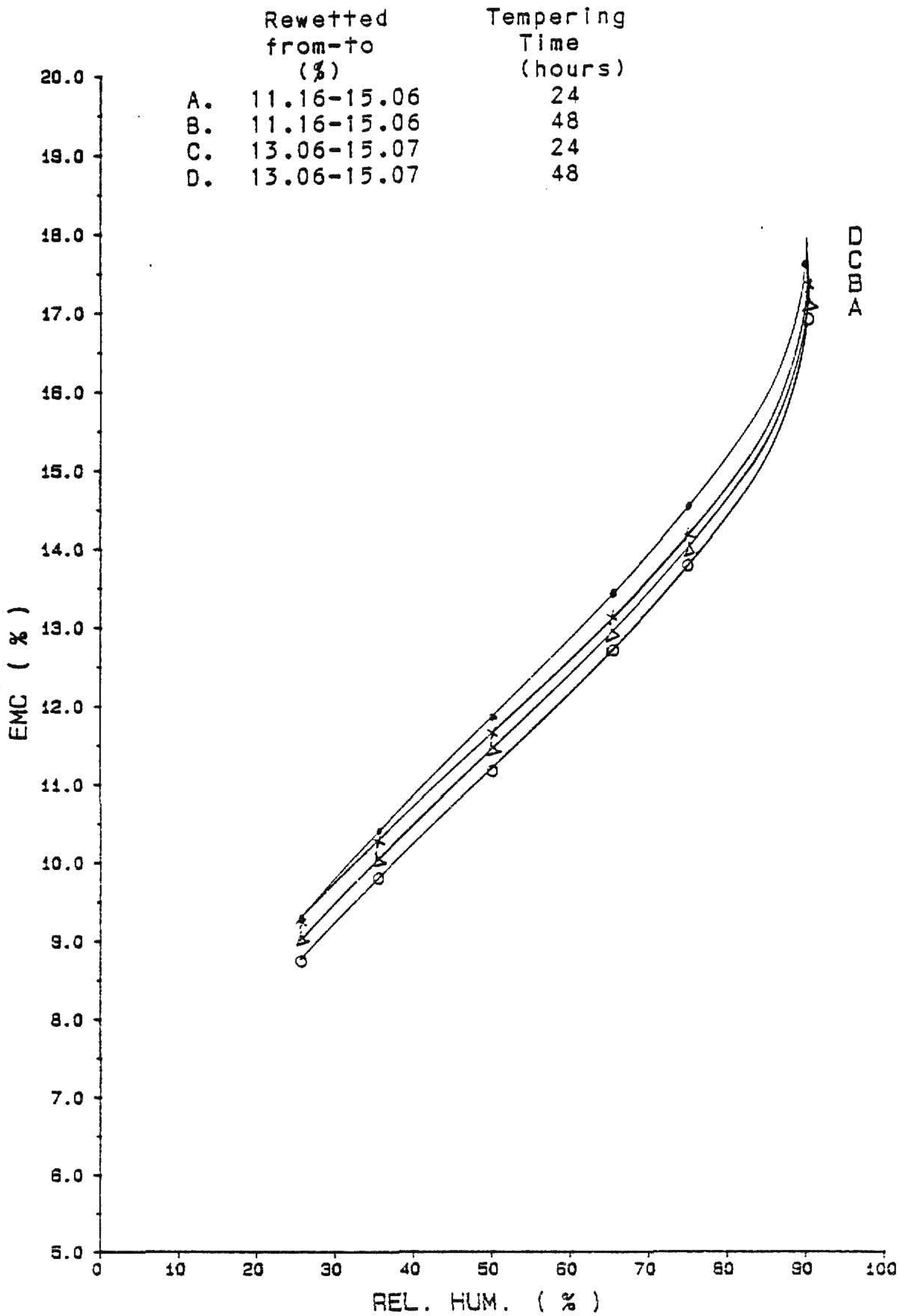


Figure 5. Isotherm curves at 25°C of corn dried at 150 F (66°C) air after rewetting.

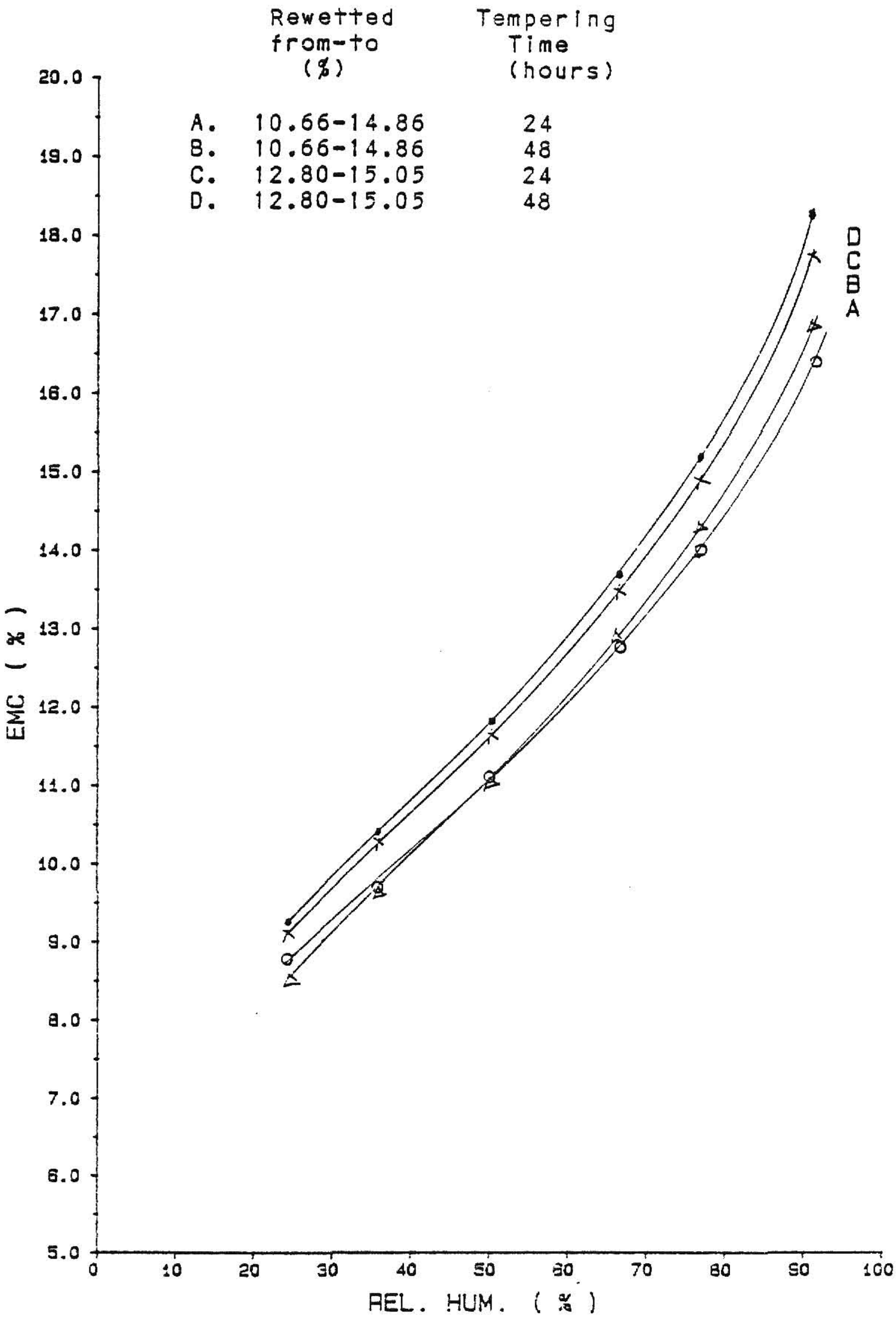


Figure 6. Isotherm curves at 25°C of corn dried at 210 F (99°C) air after rewetting.

Table 9. Analysis of Variance all Variables Included for EMC of Corn after Rewetting.

Source	D.F.	SS	F
Drying temp	5	8.1845	12.16 **
Rel.Hum.	5	2315.4611	3439.92 **
Level [a]	1	0.7096	5.27 *
Rep	1	0.0171	0.13 N.S.
Time	1	0.0564	0.42 N.S.
Temp*Rel.Hum.	25	2.9846	0.89 N.S.
Temp*Level	5	2.1194	3.15 **
Rel.Hum*Level	5	0.7560	1.12 N.S.
Error	224	30.1555	
Total	272	2360.4447	

N.S. Not Significant
* Significant at the 0.05 level
**Significant at the 0.01 level
a. In level 1 corn is rewetted from 11% to 15% m.c.
In level 2 corn is rewetted from 13% to 15% m.c.

Model: $EMC = C_1\, t + C_2\, RH + C_3\, m.c. + C_4\, Rep + C_5\, Time + C_6\, t*RH + C_7\, t*m.c. + C_8\, RH*m.c. + \epsilon$

Table 10 shows the EMC values for corn non-rewetted at 15% initial moisture content and rewetted to 15% from two moisture levels (11% and 13%) when rewetting time was 24 hours. The differences between those rewetted and non-rewetted EMC values was computed and tabulated in Table 11.

Table 12 shows a similar situation of the EMC values for corn non-rewetted at 15% initial moisture and rewetted to 15% from two moisture levels (11% and 13%) when tempering time was 48 hours. The differences between those rewetted and non-rewetted EMC values when tempering time was 48 hours was computed and tabulated in Table 13.

Table 11 for rewetting time of 24 hours shows, in general, bigger differences in EMC between rewetted and non-reweted corn than Table 13 for tempering time of 48 hours except when corn is dried at 99°C and is rewetted from 11% to 15%. For that case corn tempered 48 hours shows bigger differences in EMC than corn tempered 24 hours.

Figure 7 shows for natural air dried corn the differences between non-rewetted and rewetted conditions are small. The isotherm curve for corn at 15% before rewetting runs almost parallel to corn rewetted from 13% to 15% and tempered for 48 hours. Figure 8 for corn dried at 66°C shows bigger differences between non-rewetted and rewetted corn. The isotherm curve for initial moisture corn at 15% before rewetting is above all other isotherm curves after rewetting. Figure 9 for corn dried at 99°C shows also significant differences between rewetted and non-rewetted corn. All these differences are more noticeable in the range of 40% to 75% R.H.

In general, it can be seen that as the drying temperature increases the differences between rewetted and non-rewetted corn are more pronounced. This is so because as it was found, the EMC values for non-rewetted corn at 15% do not vary too much as the drying temperature increased but it was also found that the EMC values for rewetted corn shifted downwards as the drying temperature increased, this is why the gap between rewetted and non-rewetted corn increases with the increase of the drying temperature.

Statistical analysis was performed to reaffirm these differences. Multiple comparisons using the LSD test were performed. Cells of size 2 (i.e. 2 observations per cell) were formed (Table 14 in the Appendix). The results of these tests show that at a fixed temperature EMC of corn at 15% before rewetting and EMC of corn rewetted from 11% to 15% and from 13% to 15% differ at almost all relative humidities at the temperatures of 82°C and 99°C. EMC of corn at 15% before rewetting was in most cases higher than EMC of corn rewetted from 13% to 15% and from 11% to 15% at all temperatures.

To explain the results shown, again reference can be made to the molecular shrinkage theory. The capacity of adsorption of corn decreases when it is overdried to 13% and still more when it goes to 11%. Therefore, when corn is rewetted to 15% it tends to reach lower equilibrium moisture contents than corn that is originally at 15%.

D. Fitting of the EMC Data to Chung-Pfost Equation.

Chung and Pfost developed in 1967 a new isotherm equation, by modifying the potential theory, that may be applicable to describe the isotherms of cereal grains and their products over a wider range of relative humidities (Table 5).

This equation can be transformed to a linear form such as:

$$\ln(-RT\ln(\frac{P}{P_o}))=\ln A+BM \qquad [7]$$

A linear regression analysis was performed with EMC as the independent variable and $\ln(-RT\ (\ln P/P_o))$ as the dependent variable. The results gave values for both slope and intercept of the line. The value of the slope is constant B and the intercept is ln A in the Chung-Pfost equation.

Since it is difficult to draw conclusions from the comparison of intercepts of lines that have different slopes, the analysis of intercepts will not be performed. However, the values of constant A will be presented in most cases for completeness.

Table 10. EMC Values for Non-Rewetted Corn and Rewetted Corn for 24 hours.

Temp. of Drying	m.c. from-to (%)	Relative humidities 25%	50%	75%	90%
NAD	15	8.91	11.89	14.79	18.29
	13-15	8.62	11.50	14.58	17.13
	11-15	8.90	11.37	14.66	17.86
66°C	15	9.10	11.70	14.60	17.40
	13-15	8.64	11.44	14.31	17.34
	11-15	8.68	11.24	14.18	17.51
99°C	15	9.11	11.79	14.85	17.32
	13-15	8.76	11.41	14.17	17.38
	11-15	8.95	11.13	14.12	17.20

NAD means Natural Air Dried.

Table 11. Differences in EMC between rewetted corn with 24 hours tempering and non-rewetted corn at 15%.

Temp. of Drying	m.c. from-to (%)	Relative humidities 25% (%)	50% (%)	75% (%)	90% (%)
NAD	13-15	+0.29	+0.39	+0.21	+1.16
	11-15	+0.01	+0.50	+0.13	+0.43
66°C	13-15	+0.46	+0.26	+0.29	+0.06
	11-15	+0.42	+0.46	+0.42	+0.11
99°C	13-15	+0.35	+0.38	+0.68	-0.06
	11-15	+0.16	+0.60	+0.73	+0.12

Table 12. EMC Values for Corn Non-Rewetted and Rewetted for 48 hours.

Temp.of Drying	m.c. from-to (%)	Relative humidities 25%	50%	75%	90%
NAD	15	8.91	11.89	14.79	18.29
	13-15	9.05	11.72	14.81	17.68
	11-15	8.98	11.29	14.42	17.85
66°C	15	9.10	11.70	14.60	17.40
	13-15	8.80	11.55	14.33	17.44
	11-15	8.74	11.56	14.30	17.48
99°C	15	9.11	11.79	14.85	17.32
	13-15	9.03	11.62	14.38	17.21
	11-15	8.62	11.36	13.61	16.47

Table 13. Differences in EMC between rewetted corn with 48 hours tempering and non-rewetted corn at 15%.

Temp.of Drying	m.c. from-to (%)	Relative humidities 25% (%)	50% (%)	75% (%)	90% (%)
NAD	13-15	-0.14	+0.17	-0.02	+0.61
	11-15	-0.07	+0.60	+0.37	+0.44
66°C	13-15	+0.30	+0.15	+0.27	-0.04
	11-15	+0.36	+0.14	+0.30	-0.08
99°C	13-15	+0.08	+0.17	+0.47	+0.11
	11-15	+0.49	+0.43	+1.24	+0.85

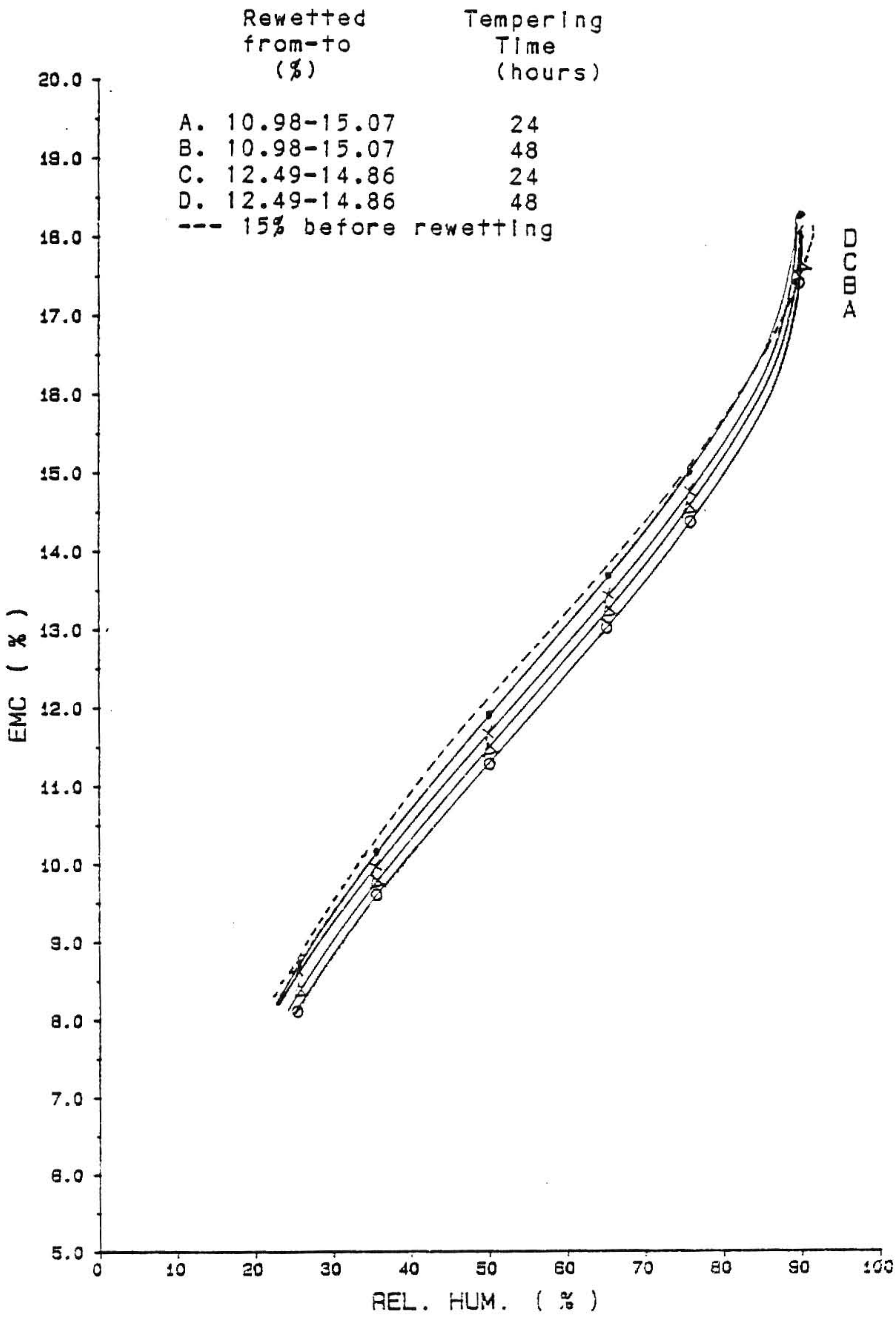


Figure 7. Isotherm curves at 25°C of naturally dried corn for non-rewetted and rewetted conditions.

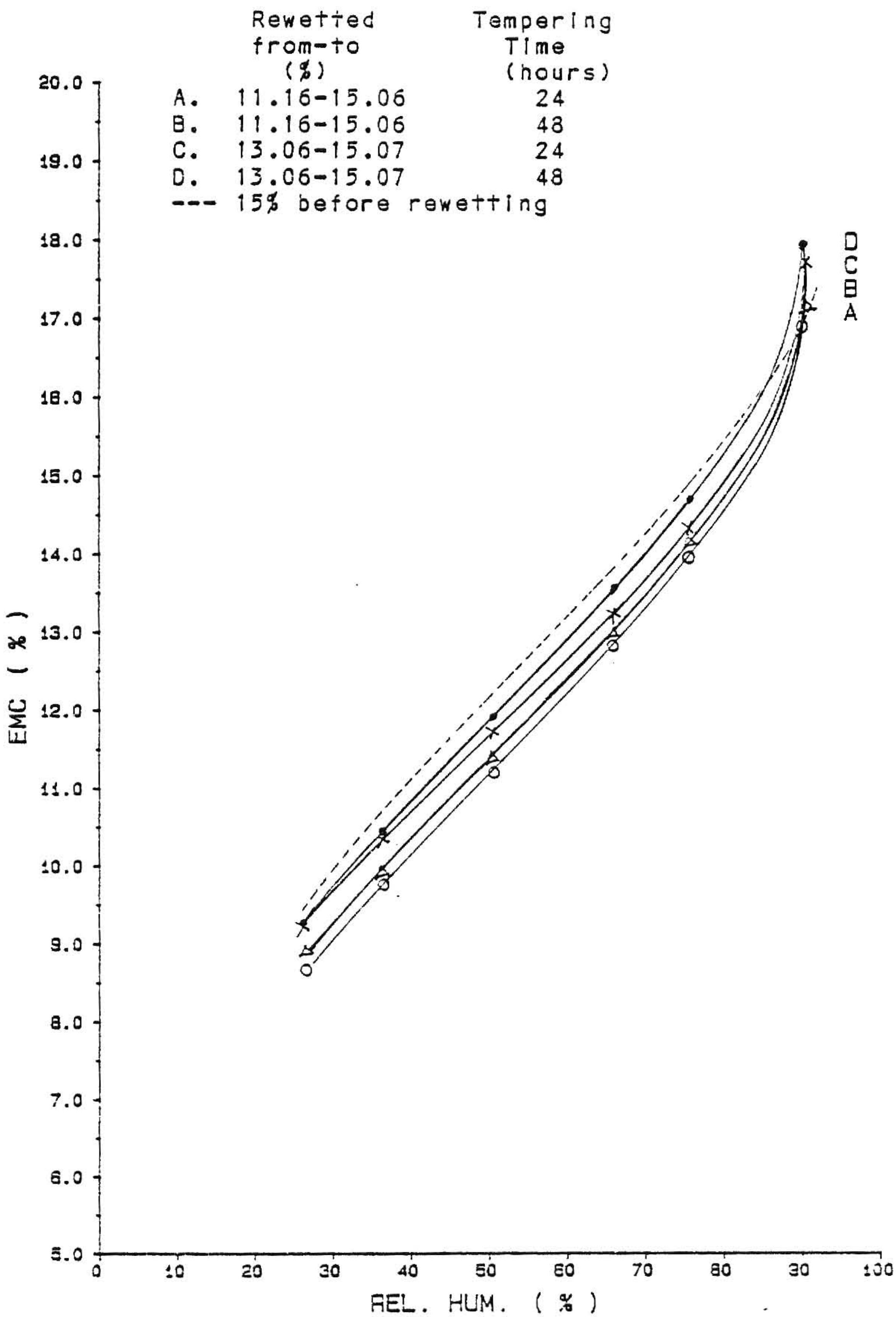


Figure 8. Isotherm curves at 25°C of corn dried at 150 F (66°C) air for non-rewetted and rewetted conditions.

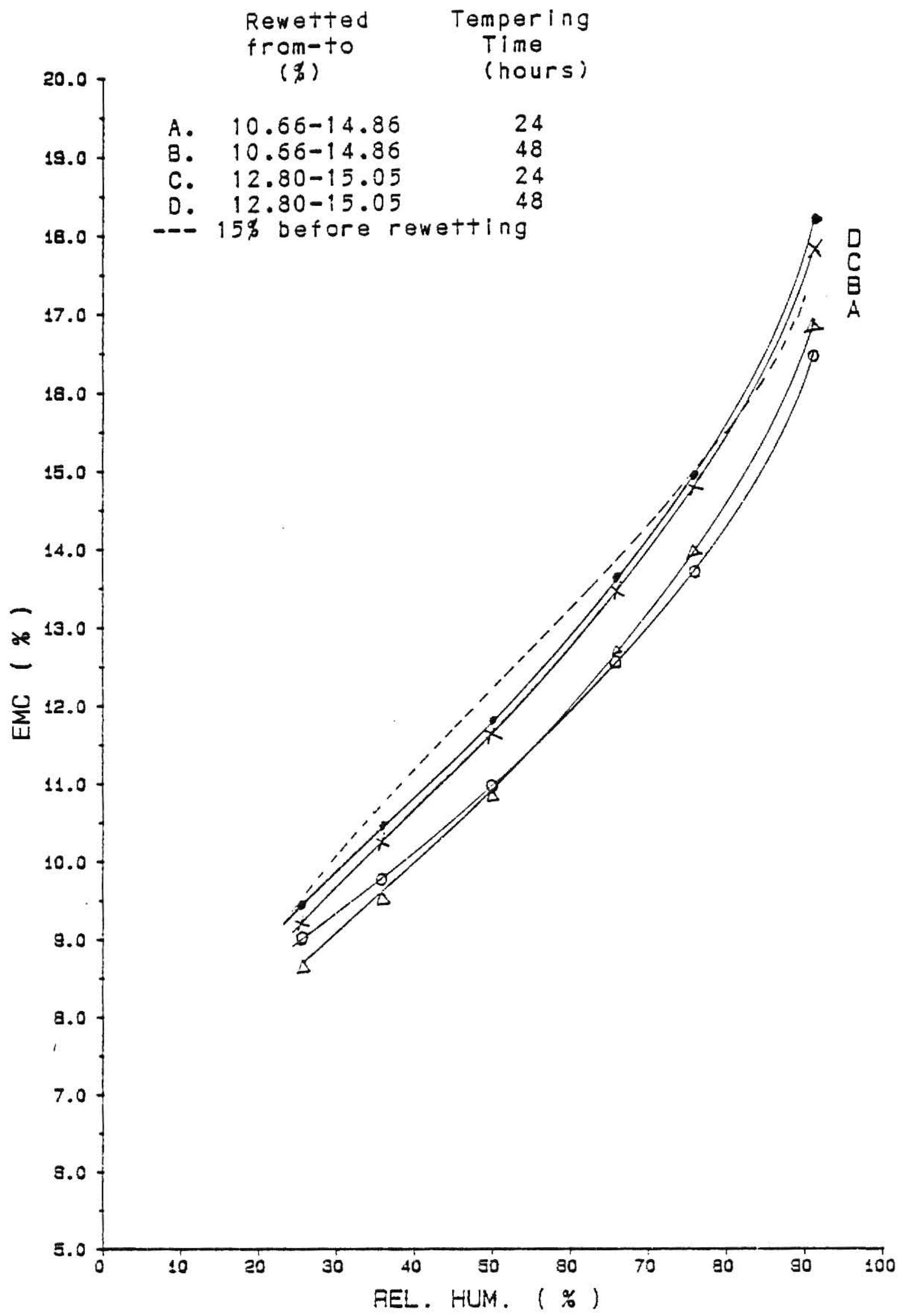


Figure 9. Isotherm curves at 25°C of corn dried at 210 F (99°C) air for non-rewetted and rewetted conditions.

For the fitting of the EMC data collected in this work to Chung-Pfost equation it was found that before rewetting three temperature groups could be formed; low, middle and high temperatures. There were three initial moisture content levels which gave 9 combinations to be analyzed. The results of the analysis are tabulated in Table 15.

In the low drying temperatures the differences in the slopes of 15%, 13% and 11% (which also defines constant B) were about one unit; in the middle drying temperatures the differences were less than one unit; and in the high drying temperatures the differences were of around two units. Since the differences in the slopes of 15%, 13% and 11% initial moisture corn were small for the low and middle drying temperatures only in the high drying temperatures 15% initial moisture corn has a significantly higher slope than 13% initial moisture corn and 13% initial moisture corn has a significantly higher slope than 11% initial moisture corn.

When analysis was made among the three temperature ranges at a fixed initial moisture content, it was found that at either 15%, 13% or 11% initial moisture corn constant B at the low drying temperatures differ considerably from constant B at the high drying temperatures (about 3 units). Then it can be found that given a initial moisture content one may determine in which temperature range corn was dried using Chung-Pfost Equation.

For the fitting of the EMC data after rewetting to Chung-Pfost equation, there were low, middle and high drying temperatures and two rewetting levels, i.e. 11-15% m.c. and 13-15% m.c. Constants A and B in Chung-Pfost equation for rewetted corn are Tabulated in Table 16. Here again the differences in the values of B among drying temperatures at a fixed rewetted level and also the differences at the same drying temperature between the two rewetting levels are less than one unit in most cases. Therefore, it is difficult to detect after rewetting whether corn was rewetted from 11% to 15% or from 13% to 15%.

When comparisons are made between rewetted and non-rewetted corn at a fixed drying temperature range (Table 17) it was found that in the low and middle drying temperatures the differences in constant B were less than one unit, but in the high drying temperature range there is up to 2.78 units of difference. Here it can be clearly shown that by comparing constant B for non-rewetted and rewetted corn in Chung-Pfost Equation one may detect differences between rewetted and non-rewetted corn if corn has been overdried with high temperature and corn is rewetted to the same moisture content of the non-rewetted corn.

II. Bulk Density Analysis

The experimental bulk density data before rewetting and after rewetting, at three different initial moisture content

Table 15. Tabulation of Constants A and B in the equation

$\ln(-RT\ln(P/Po)) = \ln A + B M$

before rewetting

m.c	Drying Temp.Range	A	B
15%	NAD & 70 F	11,313.7	-21.902*
15%	120 and 150 F	11,197.9	-21.757*
15%	180 and 210 F	15,599.6	-25.367
13%	NAD & 70 F	10,905.3	-20.764
13%	120 and 150 F	12,990.8	-22.280
13%	180 and 210 F	14,559.5	-23.833
11%	NAD & 70 F	10,157.8	-19.740
11%	120 and 150 F	13,440.1	-22.054
11%	180 and 210 F	15,275.4	-22.552

* Not Significantly different

Table 16. Tabulation of Constants A and B after Rewetting.

m.c. from-to	Drying Temp.Range	A	B
13-15%	NAD & 70 F	11,248.6	-20.917*
13-15%	120 and 150 F	12,431.6	-21.779
13-15%	180 and 210 F	13,121.4	-23.180
11-15%	NAD & 70 F	12,632.1	-21.812
11-15%	120 and 150 F	11,361.6	-20.978*
11-15%	180 and 210 F	13,095.1	-22.586

* Not Significantly Different

Table 17. Differences in constants A and B between rewetted at two moisture levels and non-rewetted at 15%.*

m.c. from-to	Drying Temp. Range	Differences ΔA	ΔB
13-15%	Low	+65.1	+0.985
11-15%	Low	-1318.4	+0.090
13-15%	Middle	-1233.7	-0.022
11-15%	Middle	-1897.2	-0.829
13-15%	High	+2478.2	+2.187
11-15%	High	+2504.5	+2.781

* All values are significantly different

levels (15%, 13% and 11% m.c.) and 6 different drying temperatures are given in Table 18 in Appendix.

A. Non-Rewetted Corn:

Three replications were performed for corn before rewetting. Statistical analysis in Table 19 shows that those three replications are not significantly different so they were averaged in Table 20. It was also found that before rewetting three drying temperature groups could be formed; low, middle and high temperatures. They are tabulated in Table 21.

At 11% m.c. corn dried at low temperatures were 1.26 lb/bu (16.21 kg/m^3) heavier than corn dried at middle temperatures and 2 lb/bu (25.74 Kg/m^3) heavier than corn dried at high temperatures. At 13% m.c. corn dried at low temperatures were 1.12 lb/bu (14.41 Kg/m^3) heavier than corn dried at middle temperatures and 1.43 lb/bu (18.27 Kg/m^3) heavier than corn dried at high temperatures. At 15% m.c. corn dried at low temperatures were 0.56 lb/bu (7.21 Kg/m^3) heavier than corn dried at middle temperatures and 1.06 lb/bu (13.65 Kg/m^3) heavier than corn dried at high temperatures.

These figures clearly reflect the fact that the effect of drying temperature on bulk density for corn dried at 15% m.c. is small but the effect of drying temperature of corn

Table 19. Analysis of Variance all Variables Included for Bulk Density of Corn before Rewetting.

Source	D.F	SS	F
Temp	5	14.9281	13.76 **
Level	2	3.2309	7.44 **
Temp*Level	10	1.9712	0.91 N.S.
Rep	2	0.4347	1.00 N.S.
Error	31	6.7267	
Total	50	27.2918	

N.S. Not Significant
** Significant at the 0.01 level
Model: B.D. = C_1 t + C_2 m.c. + C_3 t*m.c. + C_4 Rep + ∊

Table 20. Bulk Density Means before Rewetting. Pound per Bushel (Kg per cubic meter).

DRYING TEMP	LEVELS 11%	13%	15%
NAD	59.63	59.18	58.51
	(767.53)	(761.74)	(753.11)
$21^{\circ}C$	59.86	59.09	58.75
	(770.49)	(760.58)	(756.20)
$49^{\circ}C$	58.66	58.21	58.23
	(755.04)	(749.25)	(749.51)
$66^{\circ}C$	58.53	57.42	57.76
	(753.37)	(739.08)	(743.46)
$82^{\circ}C$	58.21	58.41	58.21
	(749.25)	(751.83)	(749.25)
$99^{\circ}C$	57.75	57.71	57.57
	(743.33)	(742.82)	(741.01)

Table 21. Temperature Grouping of Bulk Density Means before Rewetting. Pounds per Bushel (Kg per cubic Meter).

	[11%]	[13%]	[15%]
LOW TEMP. [NAD,21°C]	59.75	59.13	58.63
	(769.07)	(761.09)	(754.66)
MIDDLE TEMP. [49, 66, 82°C]	58.49	58.01	58.07
	(752.86)	(746.68)	(747.45)
HIGH TEMP.[99°C]	57.75	57.71	57.57
	(743.33)	(742.82)	(741.01)

overdried (11% and 13%) is noticeable. Also, in general, the lower the drying temperature, the higher the bulk density after drying.

B. Rewetted Corn:

Statistical analysis show that tempering times of 24 hours and 48 hours were not significantly different from each other (Table 22). Therefore, the data was combined and tabulated in Table 23.

From Table 23 it can be shown that, after rewetting, differences are about 1 lb/bu (12.87 Kg/m^3) between bulk density values of corn rewetted from 11% to 15% and corn rewetted from 13% to 15% at any drying temperature.

The most significant differences were among drying temperatures especially when corn was rewetted from 11% to 15% m.c. When corn dried at 21°C was rewetted from 11% to 15% m.c. it was 1 lb/bu (12.87 Kg/m^3) heavier than corn dried at 49°C and 3.12 lb/bu (40.16 Kg/m^3) heavier than corn dried at 99°C.

Comparisons are made among bulk density values at 15% before rewetting and 11-15% and 13-15% after rewetting at every drying temperature (Table 24). Table 24 shows that at 21°C and 49°C these differences were about 1 lb/bu (12.87 kg/m^3), at 99°C 15% before rewetting was 0.92 lb/bu (11.84 Kg/m^3) heavier than 13-15% and 2.14 lb/bu (27.54 Kg/m^3)

heavier than 11-15%. Therefore, only at 99°C it can be shown clearly the differences in bulk density between rewetted and non-rewetted corn.

Table 22. Analysis of Variance all Variables Included for Bulk Density of Corn after Rewetting.

Source	D.F.	SS	F
Temp	5	16.1740	43.12 *
Level	1	0.8332	11.11 N.S.
Time	1	0.4819	6.42 N.S.
Temp*Level	4	3.7267	12.42 N.S.
Temp*Time	4	3.7772	12.59 N.S.
Level*Time	1	0.5418	7.22 N.S.
Error	2	0.1500	
Total	18	25.6852	

N.S. Not Significant
* Significant at the 0.05 level
Model: B.D. = C_1 t + C_2 m.c. + C_3 Time + C_4 t*m.c. + C_5 t*Time + C_6 m.c.*Time + ϵ

Table 23. Bulk Density Means after Rewetting.

Temperature of Drying	Moisture content from-to (%)	Bulk density lb/bu (Kg/m^3)
21°C	11-15	58.55 (753.63)
	13-15	57.65 (742.04)
49°C	11-15	57.55 (740.76)
	13-15	57.10 (734.96)
99°C	11-15	55.43 (713.47)
	13-15	56.65 (729.17)

Table 24. Differences in Bulk Density between Rewetted from two moisture levels and non-rewetted at 15%.

Temp.of Drying	m.c. from-to (%)	lb/bu (Kg/m^3)
21°C	13-15	+1.10
		(14.16)
	11-15	+0.20
		(2.57)
49°C	13-15	+0.58
		(7.47)
	11-15	-0.32
		(-4.72)
99°C	13-15	+0.92
		(11.84)
	11-15	+2.14
		(27.54)

CONCLUSIONS

1. The comparison of isotherms before rewetting at three initial moisture contents (15%, 13% and 11%) shows that the differences among them start increasing as the drying temperature increases. It was found that, in general, at every drying temperature the equilibrium moisture content for 15% initial moisture corn is higher than for 11% initial moisture corn at a given relative humidity.

2. Before rewetting, 75% is the relative humidity that shows the most differences between equilibrium moisture contents reached by 15%, 13% and 11% initial moisture corn. Also, 90% is the relative humidity that shows the most differences between equilibrium moisture contents reached by different drying temperatures.

3. It was shown that if corn is overdried to about 13% or below and the drying temperature is kept above 150 F (66°C) there are significant differences among EMC of corn dried to 15%, 13% and 11% moisture contents, and EMC of corn dried at low drying temperatures and high drying temperatures.

4. After rewetting the equilibrium moisture contents reached when corn was rewetted from 11-15% were slightly lower than those reached when corn was rewetted from 13-15%. However the differences were not very

pronounced (about 0.5-1.0%).

5. In general, it was found that the EMC value of non-rewetted corn is higher than for rewetted corn. Differences in EMC values between rewetted and non-rewetted corn are more pronounced at the corn dried at high temperatures.

6. Based on this study, it can be concluded that by measuring EMC values in the range of 40% to 75% R.H. one may detect whether corn has been rewetted or non-rewetted if corn is rewetted to the same moisture content of the non-rewetted corn.

7. The experimental data obtained can be described using Chung-Pfost Equation for rewetted and non-rewetted corn. The analyses show that also by comparying constant B for non-rewetted and rewetted corn in Chung-Pfost Equation one may detect whether corn has been rewetted or non-rewetted if corn has been overdried with high temperatures and corn is rewetted to the same moisture content of the non-rewetted corn.

8. The effect of drying temperature on bulk density for corn dried to 15% moisture content is small but the effect of drying temperature on bulk density of corn overdried (11% and 13% m.c.) is noticeable. In general, the lower the drying temperature the higher the bulk density after drying.

9. After rewetting the differences on bulk density between corn rewetted from 11% to 15% and from 13% to 15% cannot be detected.

10. It appears that one cannot detect whether corn is rewetted or non-rewetted by measuring bulk density.

SUGGESTIONS FOR FURTHER RESEARCH

1. Conduct a similar study with commercially dried corn.

2. Study different rewetting methods such as a water vapor adsorption and blending dry corn with wet corn.

3. Considering factors such as; corn varieties, year and location of crop grown, and physical conditions of corn, establish an EMC Standard Curve for 15% non-rewetted corn.

4. Conduct experiment studying differences in water activity (instead of EMC) between rewetted and non-rewetted corn in order to obtain a faster way of detecting rewetted and non-rewetted corn.

5. Conduct this study on beans. In my country, for a long time it has been suspected that rewetting of beans is practiced which is illegal.

REFERENCES

1. Agricultural Engineering Yearbook. 1981. Am. Soc. Ag. Eng., St. Joseph: Michigan.

2. Becker, H. A., and H. R. Sallans. 1956. A study of the desorption isotherms of wheat at 25° and 50°C. Cer. Chem. 33: 79-91.

3. Boerner, E. G., and E. H. Ropes. 1922. The test weight of grain: A simple method of determining the accuracy of the testing apparatus. Bulletin No. 1065. U.S. Department of Agriculture. Washington D.C., 13 p.

4. Brunauer, S., P. H. Emmett, and E. Teller. 1938. Adsorption of gases in multimulecular layers. J. Am. Chem. Soc. 60: 309-319.

5. Brunauer, S. 1943. The adsorption of gases and vapors. I. Physical Adsorption. Princeton: Princeton University Press.

6. Chung, D. S. and H. B. Pfost. 1967. Adsorption and desorption of water vapor by cereal grains and their products. Parts I, II and III. Transactions of the ASAE. 10 (4):549-557.

7. Chung D. S. and J. H. Converse. 1969. Effect of moisture content on some physical properties of grain. Transactions of the ASAE. 14(4):612-614,620.

8. Dunstan, E. R., D. S. Chung, and T. O. Hodges. 1973. Adsorption and desorption characteristics of grain sorghum.

9. Eley, D. D., and R. B. Leslie. 1964. In electrical conduction of solid protein. New York: Academic Press, Inc.

10. Eley, D. D., and R. B. Leslie. 1963. In adsorption of water and solid proteins with special reference to hemoglobins. Advances in Chemical Physics. 7, New York: Interscience.

11. Grosh, G. M. and M. Milner. 1959. Water penetration and internal cracking in tempered wheat grains. Cer. Chem. 36: 260-273.

12. Hall G. E. 1972. Test weight changes of shelled corn during drying. Transactions of the ASAE. 15(2): 320-323.

13. Hall C. W. and J. H. Rodriguez Arias. 1958. Equilibrium moisture content of shelled corn. Agricultural Engineering. 39: 466-470.

14. Hart J. R. 1964. Hysteresis effects in moisture of wheat taking from the same sample but having different moisture content. Cer. Chem. 41:340-350.

15. Henderson, S. N. 1952. A Basic concept of equilibrium

moisture. Agricultural Engineering. 33: 29-32.

16. Hunt, W. H. and S. W. Pixton. 1974. Moisture its significance, behavior and measurement. In storage of cereal grains and their products. p. 303-419.

17. Mc Bain, J. W. 1910. Der mechanism der adsorption von wasserstoff durch kholenstoff. Z. Phys. Chem. 68: 471-497.

18. Milner, M. and Shellenberger, J. A. 1953. Physical Properties of wheathered wheat in relation to internal fissuring detected radiographically. Cer. Chem. 30: 202-212.

19. Perry, J. H. 1950. Chemical Engineers' Handbook. Third Edition. McGraw Hill. New York.

20. Reichenberger, L. 1982. How farmers lose millions on too dry grain. Succesful farming. Harvesting Issue June-July.

21. Ross, S. and J. P. Olivier. 1964. On physical adsorption. New York: Interscience.

22. Seehof, J. M., B. Keilin and S. W. Benson. 1953. The surface areas of protein. The mechanisms of water sorption. J. Am. Chem. Soc. 75: 24-27

23. Snedecor, G. W. 1980 . Statistical Methods. Seventh Edition. Ames: Iowa State University Press.

24. Smith, S. E. 1947. The sorption of water vapor by high polymers. J. Am. Chem. Soc. 69:649-651.

25. Thompson, and C. K. Shedd. 1954. Equilibrium moisture and heat of vaporization of shelled corn and wheat. Agricultural Engineering. 786-788. 1954.

26. U. S. Department of agriculture. 1963. Historical view of changes in the grain standards of the United States. Agricultural marketing service. Publication No. 513, 23 p.

A P E N D I X

Table 6. Experimental EMC data for non-rewetted samples.

Temp. of	Initial	Relative Humidities					
Drying	m.c.	25%	35%	50%	65%	75%	90%
NAD	10.98	8.56	9.77	11.08	12.80	14.25	17.59
	10.98	8.23	9.50	10.93	12.80	14.19	17.89
	12.49	8.92	9.76	11.49	13.07	14.61	18.13
	12.49	8.95	9.90	11.58	13.13	14.67	18.20
	14.64	8.91	10.01	11.90	13.63	14.89	18.33
	14.64	8.91	9.85	11.88	13.74	14.68	18.24
21°C	11.50	8.69	9.68	11.03	12.55	13.49	17.18
	11.49	8.70	9.78	11.19	12.60	14.04	17.21
	13.35	8.86	9.76	11.89	13.18	14.56	18.07
	13.42	8.92	9.67	11.63	13.10	14.22	18.20
	14.86	9.04	9.85	11.64	13.88	14.89	18.80
	14.87	9.09	9.86	11.51	14.16	14.86	18.89
49°C	10.98	8.65	9.74	10.90	12.39	14.01	17.52
	10.93	8.65	9.76	10.99	12.34	14.26	18.52
	12.70	9.02	9.66	11.68	12.78	14.22	16.98
	12.53	8.76	9.71	11.63	13.00	14.26	17.70
	14.86	9.24	9.72	11.85	13.67	14.99	17.93
	14.86	8.82	9.98	11.66	13.34	14.66	17.72

Table 6. Continue.

Temp.of Drying	Initial m.c.	Relative Humidities 25%	35%	50%	65%	75%	90%
66°C	10.98	8.89	9.85	11.11	12.52	13.88	17.25
	11.16	8.82	9.74	11.09	12.52	14.02	17.16
	12.96	8.76	9.96	11.55	13.00	14.40	17.54
	13.06	8.83	9.76	12.62	12.92	14.31	17.86
	14.43	9.18	10.14	11.80	13.62	14.71	17.66
	14.43	9.02	9.69	11.77	13.62	14.48	17.14
82°C	10.34	8.79	9.64	10.72	12.11	13.70	16.64
	10.96	8.88	9.64	10.98	12.21	13.48	16.84
	12.49	9.17	9.87	11.31	12.75	14.04	17.25
	12.98	8.99	9.93	11.43	12.70	13.73	16.90
	15.29	9.02	10.15	11.74	13.82	14.98	18.29
	15.29	9.51	10.26	12.23	13.84	14.82	17.52
99°C	10.34	8.51	9.31	10.39	11.71	12.91	15.99
	10.66	8.45	9.48	10.67	11.98	13.13	15.97
	12.59	8.94	9.74	11.22	12.61	13.82	16.50
	12.80	8.66	9.28	10.69	11.98	13.72	17.40
	15.01	9.03	11.25	11.85	13.55	14.74	16.77
	15.01	9.20	10.19	11.72	13.57	14.96	17.86

Table 7. Experimental EMC Data for rewetted samples.

Temp.of Drying	m.c. from-to	Tempering Time, h	Relative Humidities 25%	35%	50%	65%	75%	90%
NAD	10.98-15.07	24	8.40	9.43	10.95	13.32	14.44	17.73
	-		9.39	9.98	11.78	13.65	14.88	17.87
	10.98-15.07	48	8.98	9.89	11.70	13.46	14.38	17.45
	-		-	9.22	10.81	13.26	14.45	18.24
	12.49-14.86	24	8.69	9.62	11.62	13.27	14.70	16.97
	-		8.54	9.43	11.38	13.19	14.39	17.29
	12.49-14.86	48	8.80	9.74	11.46	12.89	14.82	17.61
	-		9.29	10.10	11.98	13.68	14.80	17.75
21°C	11.49-15.07	24	8.72	9.64	11.46	13.37	14.79	18.18
	-		8.98	10.12	11.83	13.44	14.76	17.75
	11.49-15.07	48	9.09	10.07	11.89	13.88	14.94	18.03
	-		8.92	9.76	11.83	13.55	14.78	18.10
	13.42-15.07	24	8.84	9.86	11.90	13.66	14.87	18.24
	-		8.80	10.35	12.09	13.51	14.59	16.97
	13.42-15.07	48	9.05	10.29	11.92	13.66	14.95	18.16
	-		8.77	9.44	11.47	13.29	14.35	17.20
49°C	10.93-15.50	24	9.14	10.39	11.82	13.57	14.70	17.93
	-		9.13	-	11.81	-	14.69	-
	10.93-15.50	48	9.35	10.47	12.12	13.87	14.90	17.84
	-		8.38	9.58	11.45	13.14	14.24	17.84
	12.53-14.86	24	9.43	10.24	11.42	13.60	14.74	17.46
	-		9.40	-	11.43	-	14.72	-
	12.53-14.86	48	8.30	9.52	11.22	12.95	14.09	17.70
	-		8.30	9.52	11.22	12.95	14.09	17.70

Table 7. Continue.

Temp.of	m.c.	Tempering	Relative Humidities					
Drying	from-to	Time	25%	35%	50%	65%	75%	90%
66°C	11.16-15.07	24	8.67	9.67	11.02	13.24	14.07	17.30
	-		8.68	9.70	11.45	13.20	14.16	17.72
	11.16-15.07	48	8.50	9.68	11.38	13.15	14.17	17.54
	-		8.97	9.82	11.74	13.30	14.43	17.41
	13.06-15.07	24	8.99	9.43	11.34	13.06	14.18	17.13
	-		8.29	10.60	11.54	13.05	14.44	17.55
	13.06-15.07	48	8.58	9.63	11.50	13.21	14.32	17.72
	-		9.01	9.72	11.59	13.31	14.34	17.15
82°C	10.96-15.07	24	8.63	9.45	10.94	12.74	13.78	17.00
	-		8.46	-	11.02	12.48	13.91	16.95
	10.96-15.07	48	8.43	9.29	11.12	12.77	13.97	17.41
	-		8.70	9.35	11.22	12.95	13.73	17.12
	12.98-14.43	24	8.56	9.54	11.37	12.76	13.91	17.43
	-		8.57	-	11.35	-	-	17.44
	12.98-14.43	48	8.44	9.52	11.18	13.07	14.40	17.37
	-		9.14	-	-	13.15	14.09	17.22
99°C	10.66-14.86	24	8.57	9.61	11.13	12.73	13.93	17.51
	-		9.33	9.52	11.13	13.19	14.31	16.88
	10.66-14.86	48	8.73	9.65	11.55	12.58	13.69	16.55
	-		8.51	9.14	11.17	12.58	13.53	16.38
	12.80-15.05	24	8.95	9.86	11.66	13.26	14.23	17.20
	-		8.56	9.27	11.16	12.88	14.11	17.55
	12.80-15.05	48	9.32	10.37	11.76	13.23	14.43	17.10
	-		8.73	9.70	11.48	13.04	14.33	17.32

Table 14. Fisher Least Significant Differences (LSD) Test for EMC Values for Rewetted and Non-Rewetted Corn.*

R.H.	temp.of drying	m.c. (%)	mean	grouping
90%	NAD	15	18.29	A
		13-15	17.41	B
		11-15	17.82	A B
	21°C	15	18.84	C
		13-15	17.65	D
		11-15	18.01	D
	49°C	15	17.83	E
		13-15	17.64	E
		11-15	17.86	E
	66°C	15	17.40	F
		13-15	17.43	F
		11-15	17.50	F
	82°C	15	17.91	G
		13-15	17.37	H
		11-15	17.12	H
	99°C	15	17.32	I
		13-15	17.29	I
		11-15	16.83	I
75%	NAD	15	14.79	J
		13-15	14.68	J
		11-15	14.54	J
	21°C	15	14.88	K
		13-15	14.69	K
		11-15	14.82	K
	49°C	15	14.83	L
		13-15	14.59	L
		11-15	14.64	L
	66°C	15	14.60	M
		13-15	15.10	M N
		11-15	14.21	N
	82°C	15	14.90	O
		13-15	14.20	P
		11-15	13.85	P
	99°C	15	14.85	Q
		13-15	14.25	R
		11-15	13.87	R

Table 14. Continue

R.H.	temp.of drying	m.c. (%)	mean	grouping
65%	NAD	15	13.69	S
		13-15	13.26	S
		11-15	13.41	S
	21°C	15	14.02	T
		13-15	13.53	T
		11-15	13.56	T
	49°C	15	13.50	U
		13-15	13.28	U
		11-15	13.43	U
	66°C	15	13.62	V
		13-15	13.51	V
		11-15	13.22	V
	82°C	15	13.83	W
		13-15	13.01	X
		11-15	12.74	X
	99°C	15	13.56	Y
		13-15	13.10	Y Z
		11-15	12.77	Z
50%	NAD	15	11.89	A
		13-15	11.61	A
		11-15	11.31	A
	21°C	15	11.58	B
		13-15	11.85	B
		11-15	11.75	B
	49°C	15	11.76	C
		13-15	11.53	C
		11-15	11.80	C
	66°C	15	11.79	D
		13-15	11.75	D
		11-15	11.40	D
	82°C	15	11.98	E
		13-15	11.32	F
		11-15	11.08	F
	99°C	15	11.79	G
		13-15	11.52	G
		11-15	11.25	G

Table 14. Continue

R.H.	temp.of drying	m.c. (%)	mean	grouping
35%	NAD	15	9.93	H
		13-15	9.72	H
		11-15	9.63	H
	21°C	15	9.86	I
		13-15	9.99	I
		11-15	9.90	I
	49°C	15	9.85	J
		13-15	9.88	J
		11-15	10.01	J
	66°C	15	9.92	K
		13-15	9.85	K
		11-15	9.72	K
	82°C	15	10.20	L
		13-15	9.53	M
		11-15	9.35	M
	99°C	15	10.72	N
		13-15	9.80	O
		11-15	9.48	O
25%	NAD	15	8.91	P
		13-15	8.83	P
		11-15	8.79	P
	21°C	15	9.06	Q
		13-15	8.87	Q
		11-15	8.93	Q
	49°C	15	9.03	R
		13-15	9.14	R
		11-15	9.00	R
	66°C	15	9.10	S
		13-15	8.72	S
		11-15	8.71	S
	82°C	15	9.26	T
		13-15	8.67	U
		11-15	8.56	U
	99°C	15	9.11	V
		13-15	8.89	V
		11-15	8.79	V

Tempering Time and Replications were averaged.

Table 18. Bulk Density Data

Temp. of drying	m.c. (%)	Non-rewetted Corn			Rewetted Corn	
		1st Rep lb/bu (Kg/m^3)	2nd Rep lb/bu (Kg/m^3)	3rd Rep lb/bu (Kg/m^3)	24 h lb/bu (Kg/m^3)	48 h lb/bu (Kg/m^3)
NAD	10.98	59.50 (765.86)	59.75 (769.07)	59.65 (769.79)	57.00 (733.68)	56.80 (731.10)
	12.49	59.30 (763.28)	59.35 (763.92)	58.90 (758.13)	57.40 (738.83)	57.60 (741.40)
	14.64	58.55 (753.63)	58.75 (756.20)	58.25 (749.77)		
21°C	11.50	59.60 (767.14)	60.00 (772.29)	60.00 (772.29)	59.33 (763.67)	57.77 (743.59)
	13.35	58.90 (758.13)	59.10 (760.71)	59.25 (762.64)	57.70 (742.69)	57.60 (741.40)
	14.86	59.00 (759.42)	58.65 (754.91)	58.60 (754.21)		
49°C	10.98	59.30 (763.28)	58.60 (754.27)	58.10 (747.84)	-	57.55 (740.76)
	12.70	58.90 (758.13)	58.60 (754.27)	57.14 (735.48)	-	57.10 (734.96).
	14.86	58.20 (749.12)	-	58.20 (749.12)		

Table 18. Continue.

Temp. of drying	m.c. (%)	Non-rewetted Corn 1st Rep lb/bu (Kg/m^3)	Non-rewetted Corn 2nd Rep lb/bu (Kg/m^3)	Non-rewetted Corn 3rd Rep lb/bu (Kg/m^3)	Rewetted Corn 24 h lb/bu (Kg/m^3)	Rewetted Corn 48 h lb/bu (Kg/m^3)
66°C	10.34	57.80 (743.97)	58.46 (752.47)	59.34 (763.80)	57.55 (740.76)	-
	12.96	58.90 (758.13)	57.70 (742.69)	58.68 (755.30)	58.13 (748.22)	60.46 (778.21)
	15.00	57.70 (742.69)	-	57.76 (743.46)		
82°C	11.00	58.40 (751.70)	58.15 (748.48)	58.30 (750.41)	-	-
	13.09	58.45 (752.34)	58.70 (755.56)	58.10 (747.84)	57.77 (743.59)	58.87 (757.75)
	14.97	58.76 (756.33)	57.80 (743.97)	-		
99°C	10.66	57.30 (737.54)	58.55 (753.63)	57.40 (738.83)	55.55 (715.01)	55.30 (711.80)
	12.59	57.70 (742.69)	57.85 (744.62)	57.60 (741.40)	56.43 (726.34)	56.87 (732.00)
	15.10	57.60 (741.40)	58.02 (746.81)	57.10 (734.96)		

HYGROSCOPIC PROPERTIES OF REWETTED CORN

by

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ABSTRACT

The purpose of this investigation were first, to compare isotherms for rewetted and not rewetted corn at room temperature; second, to determine the effect of three initial moisture content levels and drying temperatures on equilibrium moisture content; third, to determine the effect of moisture levels and drying temperatures on bulk density before and after rewetting, and finally, to fit the data to Chung-Pfost equation.

Fresh corn was used to obtain isotherms at room temperature by employing the sulfuric acid method. The three initial moisture content levels tested were 15%, 13% and 11%. The drying temperatures used ranged from 70 F (21^{o}C) to 210 F (99^{o}C) with natural air dried as temperature control. The relative humidities ranged from 25% to 90%. Corn was rewetted from 11% to 15%, and from 13% to 15%, at two rewetting times (24 h and 48 h). Two replications were performed. Bulk density measurements were performed prior to drying, after drying, and after rewetting.

The comparison of isotherms before rewetting at three initial moisture contents showed that the differences among them start increasing as the drying temperature increases. In general at every drying temperature the equilibrium moisture content for 15% initial moisture corn is higher than 11% initial moisture corn at a given relative humidity.

It was shown that if corn was overdried to about 13% or below and the drying temperature is kept above 66°C there are significant differences among EMC of corn dried to 15%, 13% and 11% m.c. and EMC of corn dried at low temperatures and high temperatures.

In general, it was found that the EMC value of non-rewetted corn is higher than for rewetted corn. Differences in EMC values between rewetted and non-rewetted corn are more pronounced for corn dried at high temperatures.

Based on this study it can be concluded that by measuring EMC values in the range of 40% to 75% R.H. one may detect whether corn has been rewetted or non-rewetted if corn is rewetted to the same moisture content of the non-rewetted corn.

The experimental data obtained can be described using Chung-Pfost Equation for rewetted and non-rewetted corn. By comparing constant B for non-rewetted and rewetted corn in Chung-Pfost Equation one may detect whether corn has been rewetted or non-rewetted if corn has been overdried with high temperatures and corn is rewetted to the same moisture content of the non-rewetted corn.

Before rewetting, in general, the lower the drying temperature the higher the bulk density after drying. After rewetting the differences on bulk density between corn rewetted from 11% to 15% and from 13% to 15% cannot be detected. It appears that one cannot detect whether corn is rewetted or non-rewetted by measuring bulk density.